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Evaluation of a Method for the Determination of Inorganic Carbon (Carbonates) in Solid Wastes

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EVALUATION OF A METHOD FOR THE DETERMINATION OF INORGANIC CARBON (CARBONATE) IN SOLID MATTER

A Division of Research and Development Open-File Report (RS-07-68-17)

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written by

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EVALUATION OF A METHOD FOR THE DETERMINATION OF INORGANIC CARBON (CARBONATES) IN SOLID WASTES

Donald L. Wilson*

ABSTRACT

An existing A.O.A.C. method for determining carbonate carbon was found feasible for solid waste samples. Such samples with carbonate carbon contents from 0.05 to 8.00% have been precisely and accurately analyzed.

Before the carbonate carbon contents is determined, all solid waste samples must be dried, ground to less than 2mm. and thoroughly mixed. Between 1 to 5 grams of sample were used in each determination and produced satisfactory precise and accurate data.

INTRODUCTION

The importance of a carbon analysis in some volume reduction processes used to dispose of solid wastes has been pointed out in a report on the development of a carbon and hydrogen method.[1] This carbon-hydrogen method establishes the total carbon content in solid wastes; however, probably of greater importance is knowing the quantity of carbonate carbon versus the organic carbon in the total carbon content. In the case of incineration, the efficiency of operation of an incinerator can be measured by the ability of the incinerator to dispose of organic carbon matter. On the other hand,

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high carbonate content in incinerator residue will cause hardness in leachate water.

The carbonate analysis is also necessary because the carbonate content affects the analysis of other constituents in solid wastes samples. Such as, the precision and accuracy of the ash-volatile determination (loss-on-ignition or L.O.I. at 600C) can vary with the degree of decomposition of carbonates present. Our laboratory investigations showed that during the calorific determination the degree of decomposition of calcium carbonate in incinerator residue samples depends upon the amount of combustion aid added to the sample. The carbonate content of samples must be known in order to calculate their calorific values from ultimate analyses. The oxygen content of samples is normally determined by subtracting from the volatile portion of a sample the carbon, hydrogen, nitrogen, and sulfur contents. The oxygen values may be in great error because of the oxygen combined with the carbonates and metal oxides, which resulted from the decomposition of some carbonates, in the residue left from the volatile analysis.

All carbonates react with acids and evolve carbon dioxide. Conventionally the acid most agreed upon is hydrochloric acid with some heat applied to ensure complete reaction. Application of heat can break down dicarboxylic acid (as oxalic acid at 150 C and malonic acid at 140 C) and evolve carbon dioxide[2]; however, the presence of these acids (oxalic acid is found in vegetables) in any excessive amounts is considered unusual.

Therefore, a carbonate method is basically a method for measuring carbon dioxide evolved when carbonates are acted upon by acids.

The methods in common use for the determination of carbon dioxide may be divided into two groups: direct and indirect methods.

In an indirect method, carbon dioxide is evolved and the loss in weight of the material is measured.[3, 4] In a direct method, carbon dioxide is evolved and caught in a suitable absorbing agent.[5] The direct method is much more exacting than any of the indirect methods. The direct method cited has also been applied to fertilizers, material which, like solid wastes material, is heterogeneous and contains many interfering substances.

The application of this particular direct method in analyzing solid wastes materials is described herein. The precision and accuracy of most solid wastes methods are greatly affected by sample preparation techniques. The sample preparation requirements used during the establishment of the carbonate method are the same as those discussed in the carbon and hydrogen report.

APPROACH AND RESULTS

A carbonate train was constructed (Figures 1. and 2.), with laboratory equipment presently available, to analyze the carbonate carbon as carbon dioxide. (A Knoor Alkalimeter* may be employed without changing the procedure.)Because acidic gases, other than carbon dioxide, and water affect the results in the gravimetric method, the train was constructed so that these substances could be removed. Several types of carbonates

*Product (or manufacturer) identification shown in this report does not imply endorsement by the United States Public Health Service.

may be found in solid wastes samples (Table 1), but calcium carbonate would be the most probable.

After some adaptations of the original procedure to the available equipment (already incorporated in Figure 1), the carbon content of pure calcium carbonate could be analyzed accurately and precisely.

The applicability of the method in analyzing each type* of solid wastes material for its carbonate content was established by: (a) sample weights varied to ensure complete reaction of carbonates with acid, (b) excess of interfering impurities added to ensure that they are being removed when at normal concentrations, and (c) various other forms of carbon added to ensure complete recovery of only carbonate carbon (Table 2). After the applicability of the method was established, pooled standard deviation was determined for each type of solid waste by analyzing several samples from various sources (Table 3).

Since raw refuse, residue (organics), and compost materials have low density only 1 to 3 gram sample portions are recommended for analysis. Calcium carbonate being high in carbon content (relative to solid waste material) and readily reactive to acid only 0.2 to 1.0 gram portions should be analyzed. All other type materials are analyzed in 1.0 to 5.0 gram portions. Sample portions of solid waste material less than one gram should not be analyzed because data obtained may not be reproducible or accurate.

*Types of solid wastes in this paper refer to only solid samples (domestic origin) as: raw refuse, incinerator fly ash, incinerator residue, and compost.

During the course of analyzing samples for the determination of precision (pooled standard deviation), it was noticed that solutions in the two-250ml-gas washing bottles (one containing 100ml conc. sulfuric acid and the other 20 grams silver sulfate dissolved in 100ml conc. sulfuric acid) occasionally foamed out of the bottles and into the connecting tubing. Attempts to prevent this overflow by converting to 500ml bottles only produced the need for a longer flushing time (45 minutes instead of 20 minutes) and still foam overflowed if solutions' efficiency was exhausted or the analyst was careless about the flow rate (maintained between 200 to 410 cc/min.). Therefore, the 250ml bottles were again employed with the analyst being instructed to change the solutions about each month and to take care in adjusting the flow rate.

CONCLUSIONS

An A.O.A.C. carbonate carbon method proved to be a satisfactory method for determining the measurements on 1 to 5 gram portions of solid waste samples whose carbonate carbon values were between 0.05 and 8.00 percents.

Before the carbonate carbon analysis can be performed the samples must be almost entirely dry. To ensure good precision the particle size of the samples must be less than 2 mm or pass through a #60 sieve, then thoroughly mixed before analyzing.

ACKNOWLEDGMENT

The author gratefully acknowledges the contribution of Israel Cohen who prepared many of the samples used in developing this method.

The author thanks the Division of Technical Operations, Bureau of Solid Waste Management, for the provision of samples from incinerators.

REFERENCES

1. Wilson, Donald L. Development of a Method for the Determination of Carbon and Hydrogen in Solid Wastes. Bureau of Solid Waste Management. (1970).

2. Morrison, R. T. and R. N. Boyd. ed. Effect of heat, 25.6. In Organic Chemistry. 1st ed. Boston, Massachusetts, Allyn and Bacon, Inc., 1960. p 681-682.

3. Part VIII - Lime. In Gas Chemists' Handbook. 3rd ed. p 633-635.

4. Hamilton, L. F. and S. G. Simpson ed. Determination of Carbon Dioxide, 19:10-19:11. In Quantitative chemical analysis. 11th ed. New York, New York, The Macmillan Company, 1958. p 382-387.

5. Horwitz, N. ed. Carbonate Carbon, 2.096-2.097. In Official methods of analysis of the association of official agricultural chemists. 10th ed. Washington, D. C., Association of Official Agricultural Chemists, 1965. p 25-26.

APPENDIX

Figures and Tables

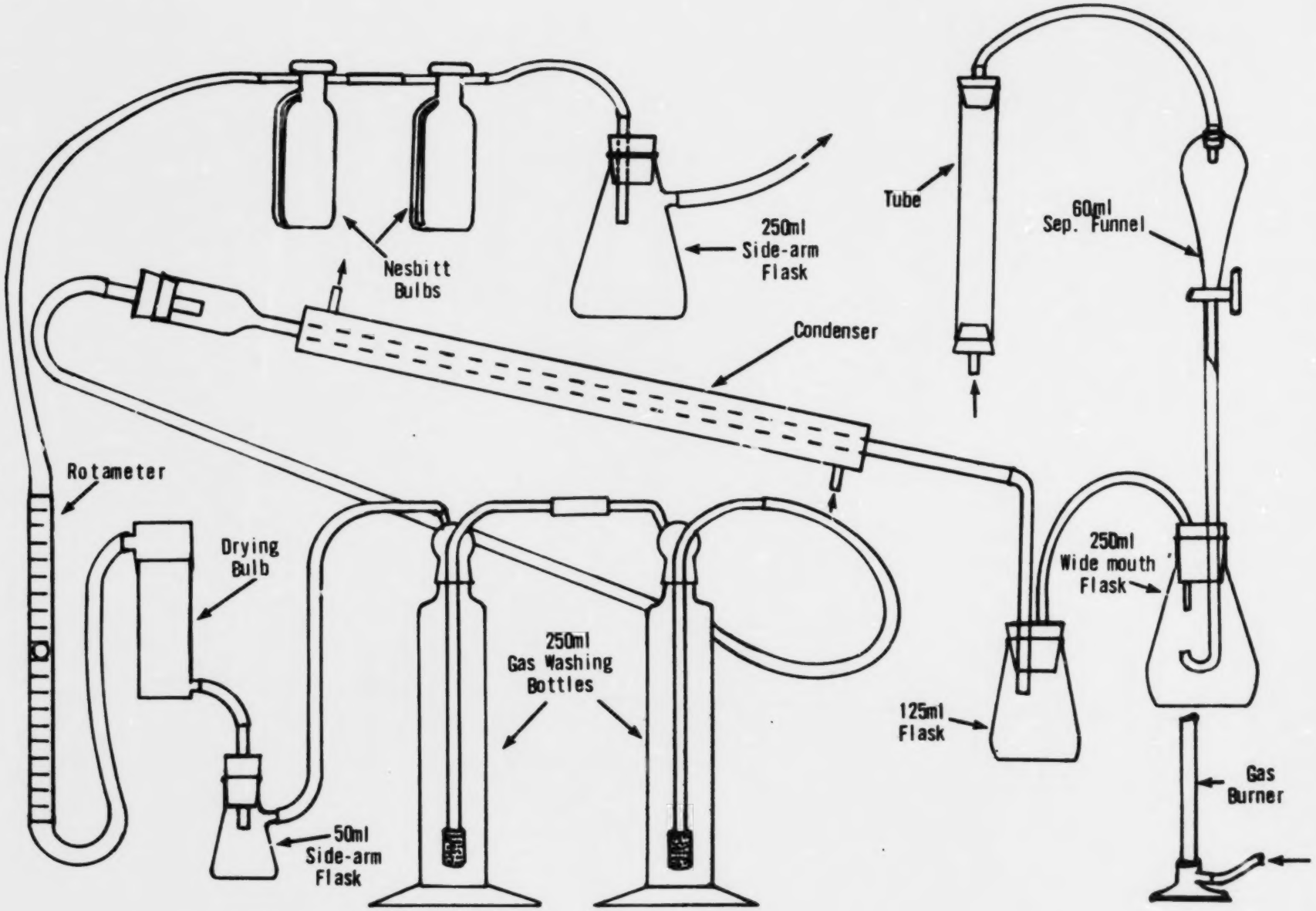

FIGURE 1. General schematic drawing of carbonate-carbon train.

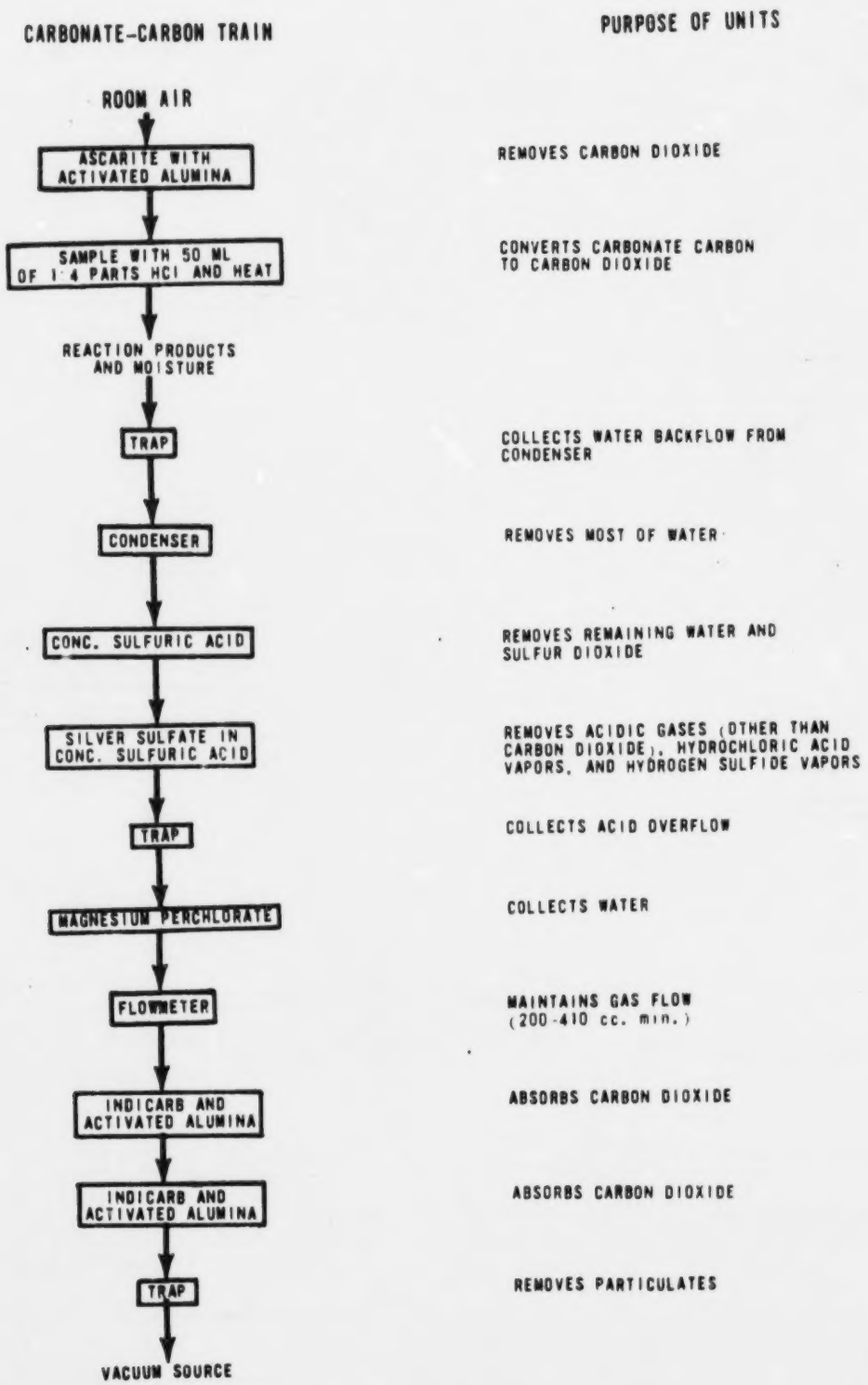

FIGURE 2 General outline of carbonate-carbon train.

TABLE 1

POSSIBLE CARBONATES IN SOLID WASTES SAMPLES FROM INCINERATORS

Type of Carbonate	Decomposition Temperature	Original Source
Calcium	825 C (aragonite) (dry begins @ 450 C) (wet begins @ 200 C)* 899 C (calcite)	eggshell, oystershell, coral, marble, chalk, tooth powders, other calcium compounds as calcium acetate and calcium oxalate
Sodium	851 C (melts) (begins @ 400 C)	glass, soap, sal soda
Magnesium	350 C to 700 C	tooth and face powders, polishing compounds, pigments
Ammonium	60 C	baking powders
Barium	1300 C	rat poison, ceramics, paints
Cupric	220 C	paints, insecticides
Lead	400 C	paints, cements, putty
Manganese	readily	pigments, varnishes
Nickel	readily	plating solutions, ceramic colors
Potassium	891 C	soap, glass, pottery
Zinc	300 C	pigments, pottery

*Friedman, Henry L. Mass Spectrometric Thermal Analysis: A Review. Thermochimica Acta, 1:199-227, 1970.

TABLE 2

EFFECT OF ADDED INTERFERING SUBSTANCES ON PERCENT INORGANIC CARBON CONCENTRATION IN SOLID WASTES

Sample Type	Additive	Percent Additive in Analyzed Sample	Percent Carbon Concentration Observed[a]	Change Possible	Change Observed
Calcium Carbonate (12.01% C)	-	-	11.97	-	-
Calcium Carbonate	Fluorine (F^-)	0.87 - 1.13	12.73	10.67 to 13.94	0.76
	Sulfur (S^{+6})	3.14 - 4.08			
	Chlorine (Cl^-)	2.04 - 2.73			
	Nitrogen (N^{+3})	4.62 - 6.00			
Calcium Carbonate	Carbon as:		11.93[b]	44.69 to 68.50	0.04
	Sucrose	15.47 - 15.73			
	Urea	4.84 - 5.10			
	Graphite[c]	24.12 - 26.38			
Raw Refuse	-	-	0.09	-	-
Raw Refuse	Fluorine (F^-)	0.64 - 0.71	0.13	7.96 to 8.82	0.04
	Sulfur (S^{+6})	2.32 - 2.58			
	Chlorine (Cl^-)	1.56 - 1.73			
	Nitrogen (N^{+3})	3.44 - 3.80			
Raw Refuse	Carbon as:		0.12	35.18 to 46.51	0.03
	Sucrose	7.53 - 16.76			
	Urea	1.45 - 5.61			
	Graphite	18.67 - 35.44			
Residue (Fines)[d]	-	-	0.65	-	-
Residue (Fines)	Fluorine (F^-)	0.52 - 0.71	0.75	6.39 to 8.75	0.10
	Sulfur (S^{+6})	1.86 - 2.56			
	Chlorine (Cl^-)	1.25 - 1.71			
	Nitrogen (N^{+3})	2.76 - 3.77			
Residue (Fines)	Carbon as:		0.70	24.53 to 29.14	0.05
	Sucrose	9.72 - 11.63			
	Urea	3.19 - 4.21			
	Graphite	10.72 - 15.21			

TABLE 2 (Continued)

EFFECT OF ADDED INTERFERING SUBSTANCES ON PERCENT INORGANIC CARBON CONCENTRATION IN SOLID WASTES

Sample Type	Additive	Percent Additive in Analyzed Sample	Percent Carbon Concentration Observed[a]	Change Possible	Change Observed
Residue (Organics)[e]	-	-	7.91	-	-
Residue (organics)	Fluorine (F^-)	0.52 - 0.58	8.34	6.39 to 7.24	0.43
	Sulfur (S^{+6})	1.86 - 2.12			
	Chlorine (Cl^-)	1.25 - 1.42			
	Nitrogen (N^{+3})	2.76 - 3.12			
Residue (Organics)	Carbon as:		8.10	40.32 to 43.15	0.19
	Sucrose	9.75 - 10.42			
	Urea	2.99 - 3.94			
	Graphite	26.30 - 29.89			
Fly Ash	-	-	1.31	-	-
Fly Ash	Fluorine (F^-)	0.56 - 0.67	1.26	6.94 to 8.32	0.05
	Sulfur (S^{+6})	1.02 - 1.22			
	Chlorine (Cl^-)	1.36 - 1.63			
	Nitrogen (N^{+3})	0.91 - 1.09			
Fly Ash	Carbon as:		1.33	22.15 to 29.64	0.02
	Sucrose	8.06 - 14.70			
	Urea	4.14 - 6.49			
	Graphite	7.44 - 10.80			

[a] Values represent the average of at least three individual determinations.
[b] Concentration of carbon in solid wastes material after substracting theoretical amounts of carbon added.
[c] Since graphite is not pure, it was ignited in air at 1150 C to determine the percent ash impurities.
[d] "Fines" are materials remaining after most of the readily combustible substances have been removed by manual sorting. The sorting was performed at the incinerator sites and a 1/2 inch sieve was employed to assist in the operation.
[e] "Organics" are mostly the readily combustible materials. Unlike "fines" these materials are usually retained on a 1/2 inch sieve.

TABLE 3

STANDARD DEVIATION[a] OF THE CARBON (CARBONATE) DETERMINATION ON CALCIUM CARBONATE AND SOLID WASTES

Type of Sample	Number of Samples	Carbon		Per Cent Carbon Range
		Duplicates	Triplicates	
Calcium Carbonate[b]	3	-	0.18	-
Residue (Fines)	12	0.01	0.02	0.05 to 0.69
Residue (Organics)	4	0.18	0.15	0.59 to 8.00
Fly Ash	6	0.13	0.15	0.70 to 1.39
Raw Refuse	13	0.08	0.07	0.06 to 0.96

[a]A variance estimate can be calculated from the duplicate (or triplicate) set of observations for each sample. The pooled variance is essentially an average of all such estimates for samples of a given type. It is assumed that a single underlying variance exists for all samples of a given type. The pooled variance is then the best estiamte of this underlying variance. The pooled standard deviation is the square root of the pooled variance and is used to estimate the underlying standard deviation.

[b]American Chemical Society grade.